Iodinated aluminum(III) corroles with long-lived triplet excited states

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Materials and Methods

Physical Methods

^{1}H and ^{19}F NMR spectra at room temperature (r.t.) were recorded on a Bruker Avance III 400 spectrometer equipped with a 5 mm, automated tuning and matching broad band probe (BBFO) with z-gradients, operating at 400.4 MHz for ^{1}H and 376.7 MHz for ^{19}F, respectively. Chemical shifts are reported in ppm relative to the residual hydrogen atoms in the deuterated solvent benzene-d_6 (δ=7.15). ^{1}H NMR spectra at low temperature were recorded on Bruker Avance III 600 spectrometer, operating at 600.6 MHz for ^{1}H and 565.0 MHz for ^{19}F, respectively. Chemical shifts are reported in ppm relative to the residual hydrogen atoms in the deuterated solvent toluene-d_8 (δ=2.09).

Absorption spectra of the samples were measured on an HP 8453 diode array spectrophotometer.

Mass spectra were measured on Waters Micromass Maldi Micro MX mass spectrometer, using TOF electron negative mode.

Two subsequent crystallizations from benzene/pentane and benzene/heptane, including a few drops of pyridine, afforded X-ray quality crystals. The diffraction measurements were carried out on a Nonius Kappa CCD diffractometer, using graphite monochromated Mo Kα radiation (λ = 0.7107 Å).

Steady-state and time-resolved emission measurements were conducted at the Beckman Institute Laser Resource Center. Emission spectra were recorded on samples dissolved in benzene or pyridine solution to measure the emission of the 5- and 6-coordinate compounds, respectively. Samples were degassed by three freeze-pump-thaw cycles. Room-temperature steady-state emission spectra were recorded on a Jobin Yvon Spex Fluorolog-3-11. Sample excitation was achieved via a xenon arc lamp with a monochromator providing wavelength selection. An excitation wavelength of 432 nm was employed, and emission was recorded between 550 and 750 nm. Slits of 2 nm bandpass were used for excitation and emission. Right angle light emission was sorted using a monochromator and fed into a Hamamatsu R928P photomultiplier tube with photon counting. Quantum yields were measured by comparing the absorption and integrated emission values of the complexes in benzene or pyridine at a variety of absorption values from 0.02 to 0.2 versus a zinc tetraphenylporphyrin standard in benzene. The temperature dependence of the quantum yield was measured by examining the intensity of emission in benzene over a range of -20 to 50^{o}C. Comparative solution and glass temperature measurements were performed on the complex in toluene solution (RT) or glass (77 K) with an excess of imidazole to guarantee essentially 100% 6-coordinate sample in solution. The 514.7 nm line of an argon ion laser (Coherent Inova 70) was used to excite samples, and right angle emission was collected via with a Melles Griot Fiber Optic Spectrometer (MGSPEC-2048-SPU).

For time-resolved measurements, samples were excited at 593 nm. Pulses of 8 ns duration from the third harmonic of a Q-switched Nd:YAG laser (Spectra-Physics Quanta-Ray PRO-Series) operating at 10 Hz were used to pump an optical parametric oscillator (OPO, Spectra-Physics Quanta-Ray MOPO-700) to provide laser pulses at 593 nm. Pulses from a xenon lamp were detected with a photomultiplier tube (PMT, Hamamatsu R928) to measure the transient rise in absorption at 475 and the transient bleach at 432 nm (whose lifetimes correspond to each other and to that of the excited state). Transient absorption traces were fit to an exponential decay function in the Igor data-processing program. PMT current was amplified and recorded using a transient digitizer (Tektronix DSA 602).

Materials

Silica gel 60 (230-400 mesh) was used for column chromatography. Reagents (Aldrich) and solvents were used without further purification. The Al corrole **1-Al** was synthesized as previously reported[6].

Calculation of equilibrium constant for the association reaction of mono- and bis-pyridine coordinated forms of **4-Al**

$$\textbf{4-Al}(py) + \text{pyridine} \overset{K}{\rightleftharpoons} \textbf{4-Al}(py)_2 \qquad (1)$$

$$K = [\textbf{4-Al}(py)_2]/[\ \textbf{4-Al}(py)][\ \text{pyridine}] \qquad (2)$$

The ε values of **4-Al**(py) and **4-Al**$(py)_2$ were obtained from the spectra of isolated **4-Al**$(py)_2$ in toluene and toluene/5% pyridine, respectively. These ε values were used for farther calculations.

The equilibrium constant (**K**, eq. 1-2) was obtained by titration curves at 636 nm, where the difference in ε values between the 5-coordinate and the 6-coordinate **4-Al** differ the most (Fig S3).

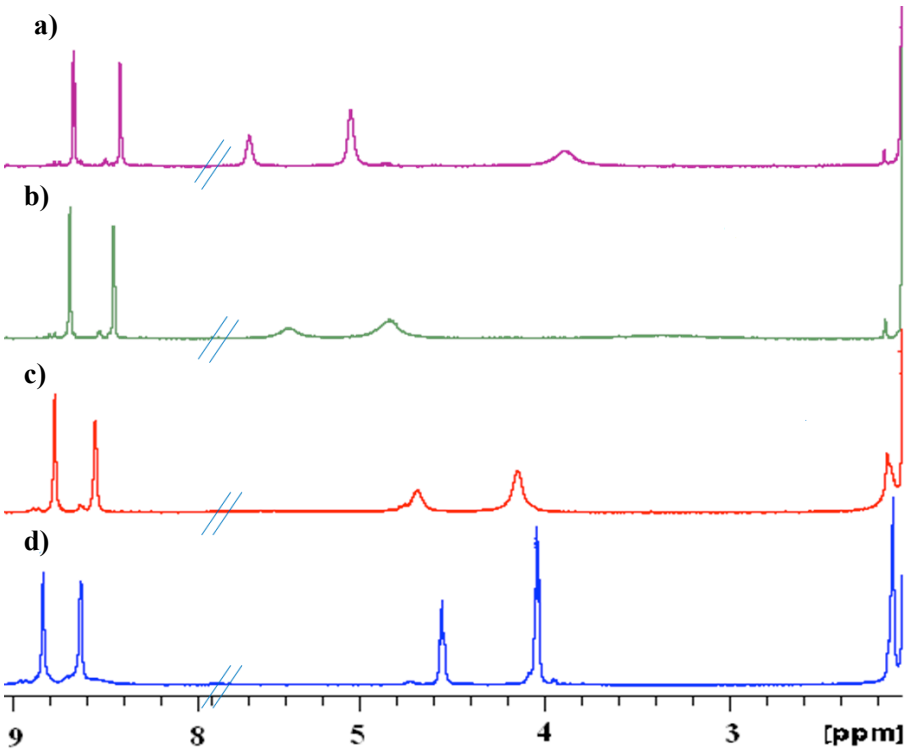


Figure S1. Dynamic ^{1}H NMR spectrum of **4-Al** in toluene-d_8: a) 300 K, b) 270 K, c) 231 K, c) 209 K.

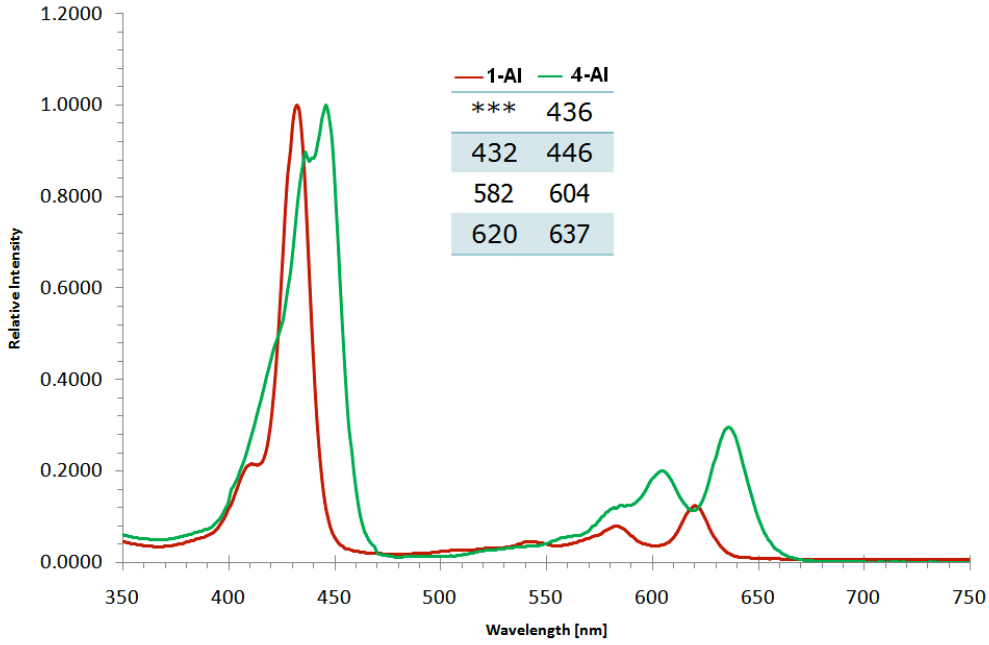


Figure S2. UV-vis absorption spectrum of **1-Al** and **4-Al** in pyridine at r.t.

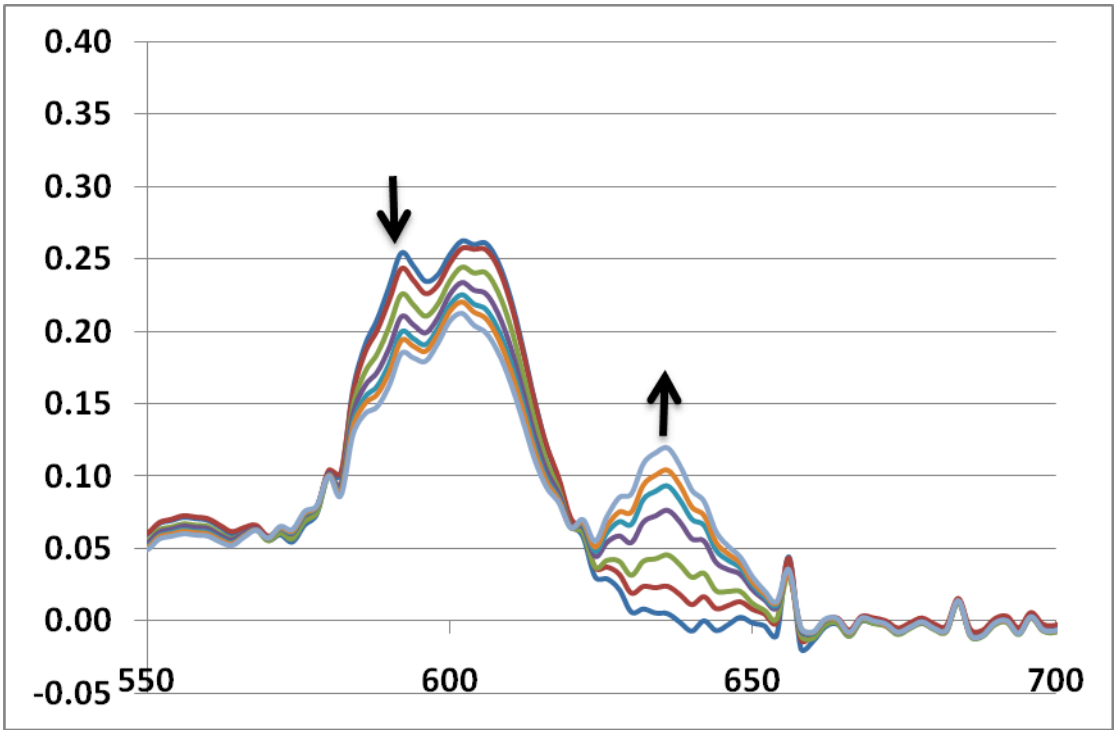
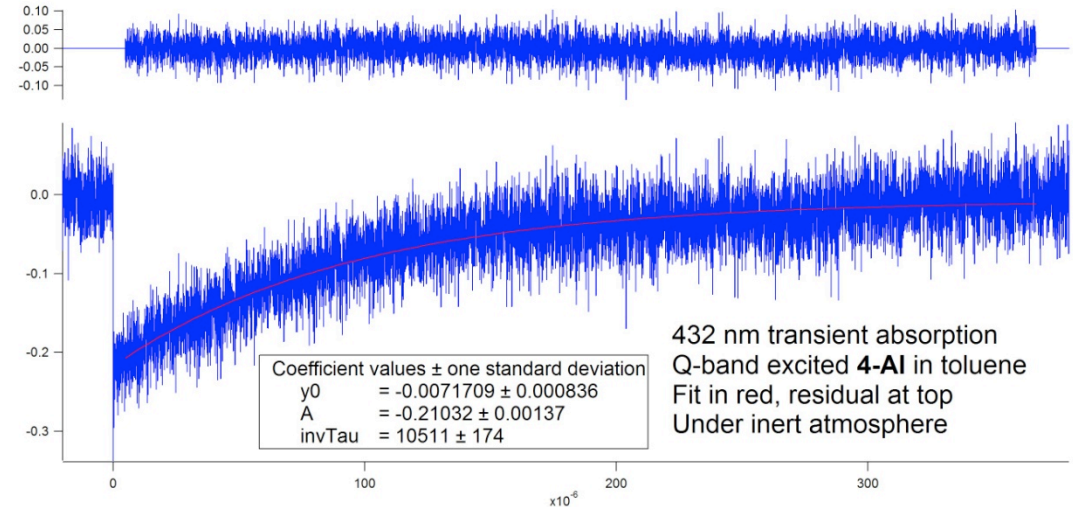
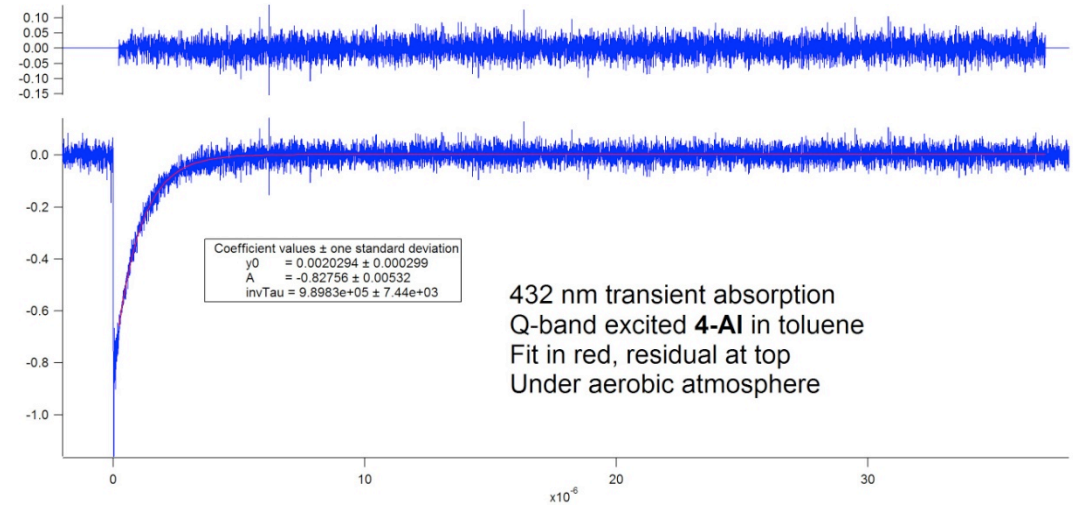
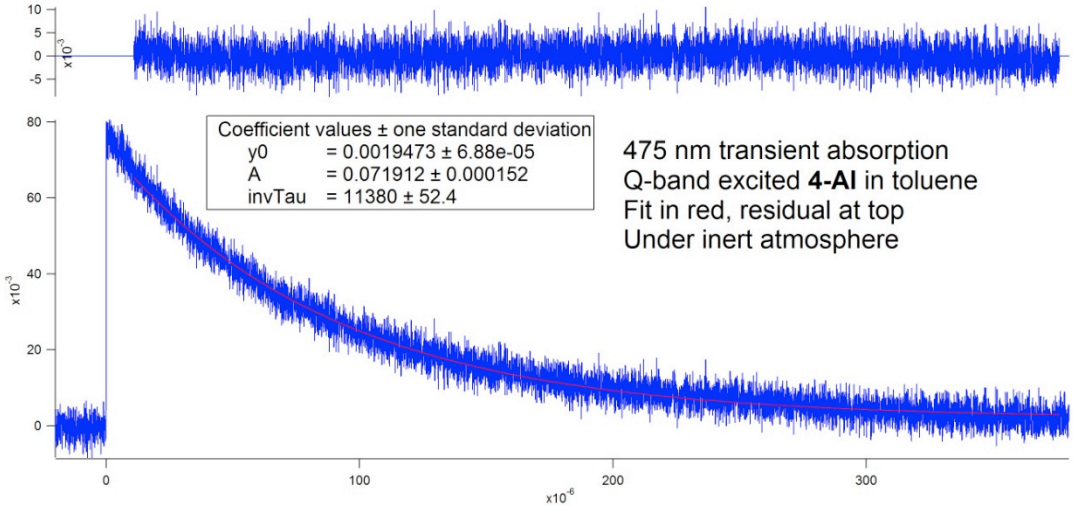


Figure S3. Titration of an 8.5 µM toluene solution of **4-Al** by pyridine (0-3 mM).


Coefficient values ± one standard deviation
y0 = -0.0071709 ± 0.000836
A = -0.21032 ± 0.00137
invTau = 10511 ± 174
432 nm transient absorption
Q-band excited **4-Al** in toluene
Fit in red, residual at top
Under inert atmosphere
x10-6


Coefficient values ± one standard deviation
y0 = 0.0020294 ± 0.000299
A = -0.82756 ± 0.00532
invTau = 9.8983e+05 ± 7.44e+03
432 nm transient absorption
Q-band excited **4-Al** in toluene
Fit in red, residual at top
Under aerobic atmosphere
x10-6


Coefficient values ± one standard deviation
y0 = 0.0019473 ± 6.88e-05
A = 0.071912 ± 0.000152
invTau = 11380 ± 52.4
475 nm transient absorption
Q-band excited **4-Al** in toluene
Fit in red, residual at top
Under inert atmosphere
x10-3
x10-6

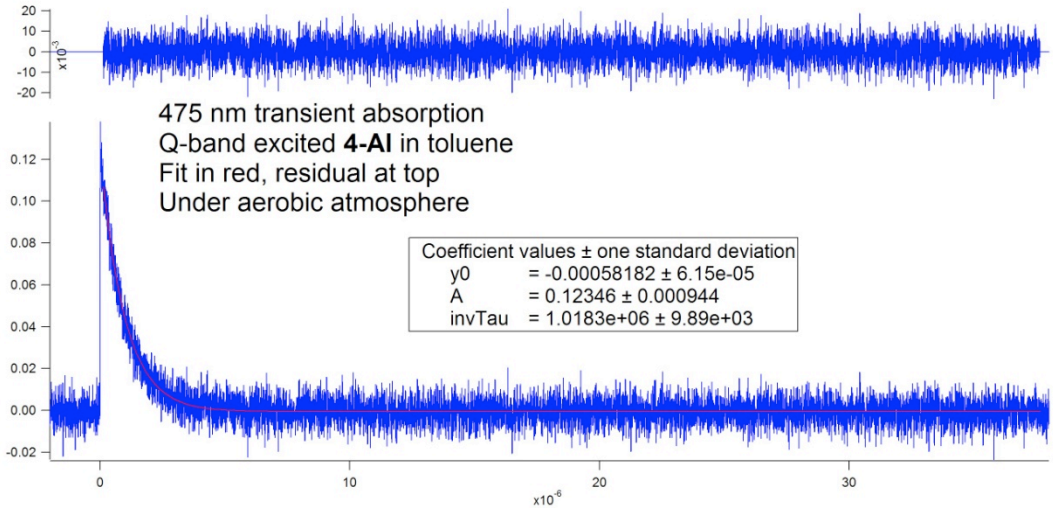


Figure S4. Illustration of the decreased lifetime of the excited state of **4-AI** in toluene upon exposure to atmosphere.